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ESTIMATION OF GRAIN BOUNDARY DIFFUSIVITY IN NEAR-ALPHA TITANIUM POLYCRYSTALS (PREPRINT)

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14. ABSTRACT

The role of enhanced grain boundary diffusivity in high-temperature diffusion of interstitial elements through metals is widely recognized but poorly characterized in most materials. This paper summarizes an effort to estimate grain boundary diffusivity of oxygen in a near-alpha titanium alloy, Ti-6Al-2Sn-4Zr-2Mo-0.1Si, by explicitly incorporating microstructure obtained from electron backscatter diffraction into an analytical model. Attention is focused on near-surface diffusion behavior contributing to the rapid ingress of oxygen and possible crack initiation in high-temperature environments.

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Estimation of Grain Boundary Diffusivity in Near-α Titanium Polycrystals

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Abstract

The role of enhanced grain boundary diffusivity in high-temperature diffusion of interstitial elements through metals is widely recognized but poorly characterized in most materials. This paper summarizes an effort to estimate grain boundary diffusivity of oxygen in a near-α titanium alloy, Ti-6Al-2Sn-4Zr-2Mo-0.1Si, by explicitly incorporating microstructure obtained from electron backscatter diffraction into an analytical model. Attention is focused on near-surface diffusion behavior contributing to the rapid ingress of oxygen and possible crack initiation in high-temperature environments.

Keywords: Grain boundary diffusion; oxidation; micromechanical modeling; electron backscattering.

The objective of the present study is to characterize the role of grain boundary diffusivity on the ingress of oxygen into α + β processed Ti-6Al-2Sn-4Zr-2Mo-0.1Si (Ti-6242S) in a high temperature environment, and to estimate appropriate diffusion properties for use in numerical simulations. The oxygen-rich regions are associated with a significant loss in tensile ductility [1] which, under mechanical or acoustic loading, allows for easy crack initiation [2]

The material of interest, the near-α alloy Ti-6242S, is a two phase titanium alloy consisting of hexagonal close packed α phase and body centered cubic β phase. Electron backscatter diffraction (EBSD) was used to investigate the microstructure and populate the finite element model. As evident in Figure 1, the material consists of about 91 percent α phase, with the remainder being β phase. The microstructure consisted of primarily globular α with a mean diameter of 6 μm, although there was a small fraction of acicular secondary α which can be seen in Figure 1. The β phase was located primarily at α triple points and thus did not form interconnected channels through the material. In order to estimate grain boundary diffusivity via analytical modeling, it was first necessary to obtain experimental concentration profiles. For this purpose, wavelength dispersive spectroscopy (WDS) was used to determine the oxygen penetration depths in samples subjected to a variety of exposure times. Although it cannot provide an accurate concentration of ultra light elements, the energy resolution of WDS is sufficient to separate peaks that normally overlap with energy dispersive spectroscopy. Thus, the total number of O Kα counts can be obtained as a function of position from the surface making this technique useful for establishing an effective oxygen composition profile for a particular

exposure time. Because the oxygen concentration trends to a consistent value in the bulk, the near-surface O gradient can be measured.

Two-dimensional finite element models have been generated directly from the EBSD scan data. The nodal spacing in the model is 85-100 nm, with grain boundaries represented by one-dimensional elements having a uniform assigned thickness. A 35-μm square region of the sample is represented in the models. The grain boundary geometry is represented to the full accuracy of the EBSD scan data, with the mesh following the grain boundaries precisely. Diffusion properties of the α and β phases, which are represented explicitly in the model, are taken to be spatially isotropic, and represented by models of the form

$$D_i(T) = D_0^i \, e^{-Q_i/RT} \qquad (1)$$

in which i = α or β is the material phase. Model constants are taken from the survey by Liu and Welsh [3,4] (D_0^α =0.45 cm^2/sec, Q_α =200 kJ/mol, D_0^β =1.6 cm^2/sec, Q_β =202 kJ/mol), giving D_α=2.105×10^{-4} μm^2/sec and D_β=5.765×10^{-4} μm^2/sec for the 650°C condition considered below.

The significance of grain boundary diffusion depends upon the product of the diffusivity and the effective grain boundary thickness; here we will characterize the relative diffusivity of the grain boundary in terms of the ratio

$$k = D_{GB} t_{GB} / D_\alpha d \qquad (2)$$

in which d is the mean grain diameter (about 6.5 μm for the samples considered herein). The quantity k is proportional to the ratio of diffusivity times area for the grain boundary and the α phase in a representative cross section [5]. Although the grain boundary diffusivity is likely to depend upon the surrounding phases, and may be affected by crystallographic misorientation and the associated presence of dislocations, we assume a single value of this property because of the lack of any experimental data.

To identify the grain boundary diffusivity ratio of eqn. (2), we first perform a series of simulations for several assumed values of k, and compare these with the experimentally determined relative concentration map for the maximum exposure time of 420 hours. Figure 2 shows that a value of k = 150,000 provides a reasonable representation of the measured data at this time. In the plot, a normalized concentration value equal to unity represents the unexposed oxygen content, about 0.107 wt. percent, as determined by x-ray fluorescence spectroscopy. The maximum value of two corresponds to the concentration at the exposed surface of the specimen. It should be noted that, since the diffusion model is linear, the oxygen content above the nominal value in the model depends linearly upon the assumed concentration at the surface.

Both the predicted and measured oxygen concentration profiles exhibit oscillations versus depth, but the nature of these two behaviors is different. In the case of the WDS data, the electron probe interaction volume is of the order of 3μm and thus may include contributions from

multiple constituents if the beam were placed on a grain boundary, for example. Moreover, the concentration profile for each exposure time shown in Figure 2 is the average of 20 independent line scans on the sample which introduces further variability. The model data in Figure 2 are averages taken along lines perpendicular to the specimen surface at regular intervals into the depth. For large values of the diffusivity ratio k, grain boundary diffusion is much faster than diffusion through the grains, so it is common for individual grains to be surrounded by a heightened concentration of oxygen which then diffuses slowly into the interior of the grain. This effect can be seen clearly in Figure 3, which shows predicted concentration maps at three equally-spaced exposure times for the case of k = 150,000. Oxygen concentrations are normalized as in Figure 2. The resulting average concentration versus depth is non-monotonic. For lower values of the ratio k, where grain boundary diffusion rates are more similar to those in the grain interiors, this effect is less pronounced, as can be seen in Figure 2. It should be noted that the lower boundary of the model has a no-flow condition imposed, which may affect the concentration values slightly within a few microns of this edge. To simulate longer exposure times, either a larger segment of the specimen must be modeled or the lower surface boundary condition modified.

As a test of the model correlation, we use the selected properties (corresponding to k = 150,000) and compare average concentration profiles with measured data for several exposure times; see Figure 4. The agreement is quite reasonable, given the variability in the experimental data and the relative simplicity of the diffusion model. Further work is needed to sharpen our ability to derive qualitative information from the experimental images, and to refine the analytical model, which is temperature-dependent but otherwise strictly linear.

Correlation of microstructural imaging data and two-dimensional computational results suggest that average grain boundary diffusivity in Ti-6242S at 650°C is on the order of 10^5 times larger than that of the base material. Similar values have been reported for aluminum wire [6] and polycrystalline nickel [7]. The combined experimental-analytical approach used in this study provides a means for a reasonable order-of-magnitude estimation of the influence of enhanced diffusion within the grain boundary in polycrystalline materials whose basic diffusion properties are known.

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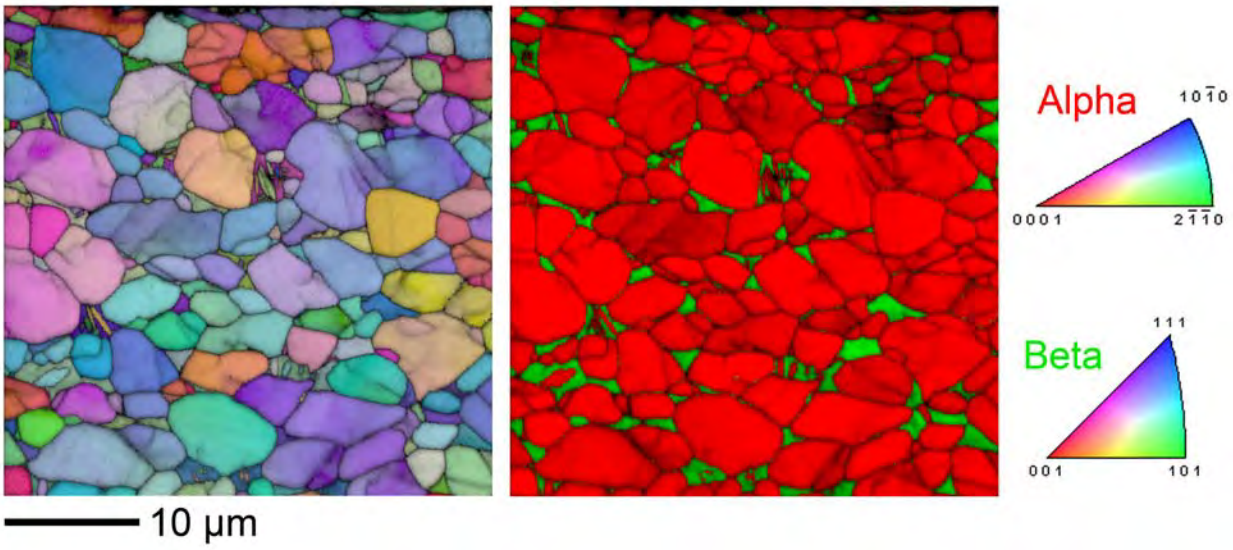
Figure Captions.

Figure 1. Microstructure at the surface of the Ti-6242S sample represented as a crystal orientation map (left) and phase map where the α phase is red and the β phase is green. The standard triangles depict the orientation of the α and β phases within the orientation map.

Figure 2. Normalized oxygen concentration profile at 420 hours (obtained by WDS) versus predictions for various grain boundary diffusivity ratios.

Figure 3. Predicted normalized oxygen concentration maps at 140, 280, and 420 hours.

Figure 4. Oxygen concentration profiles at selected times for diffusivity ratio k = 150,000.



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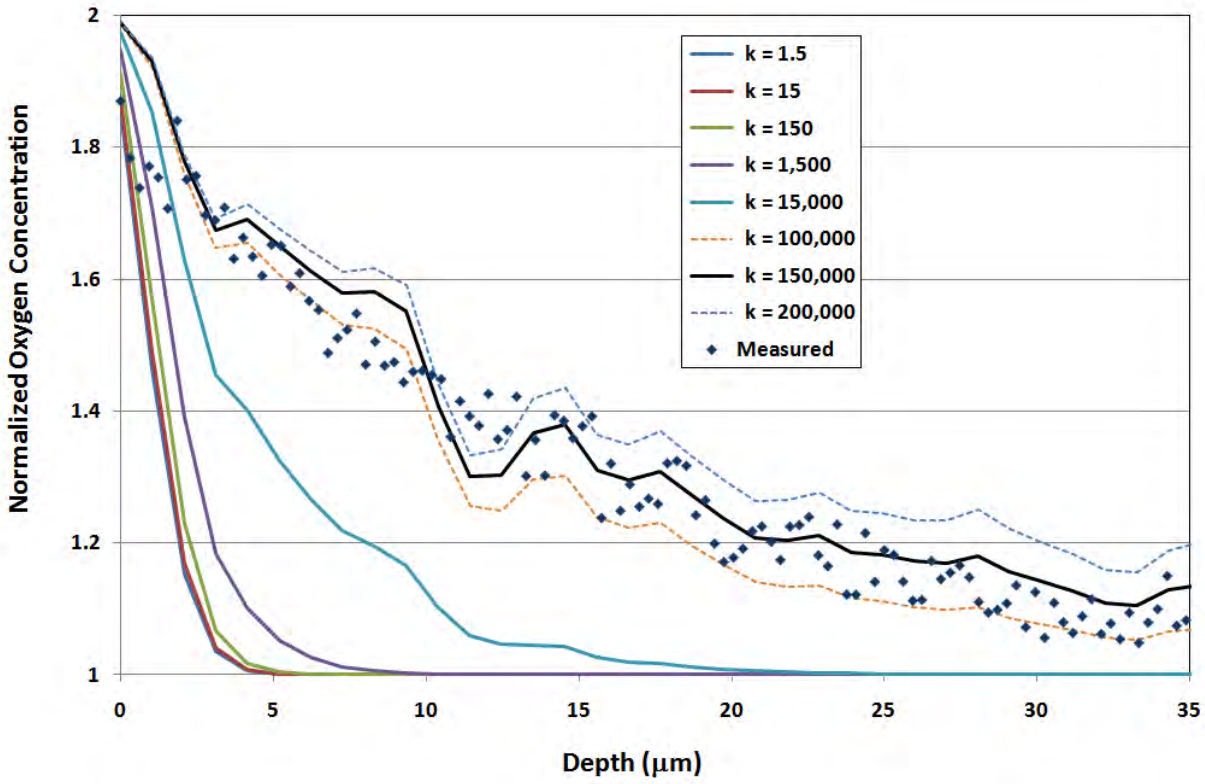

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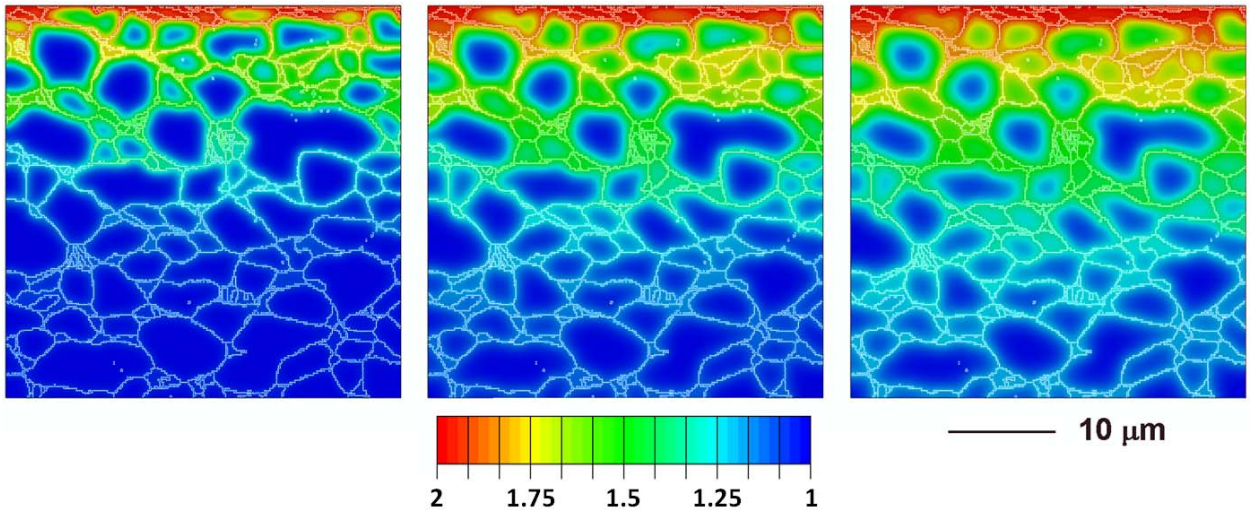

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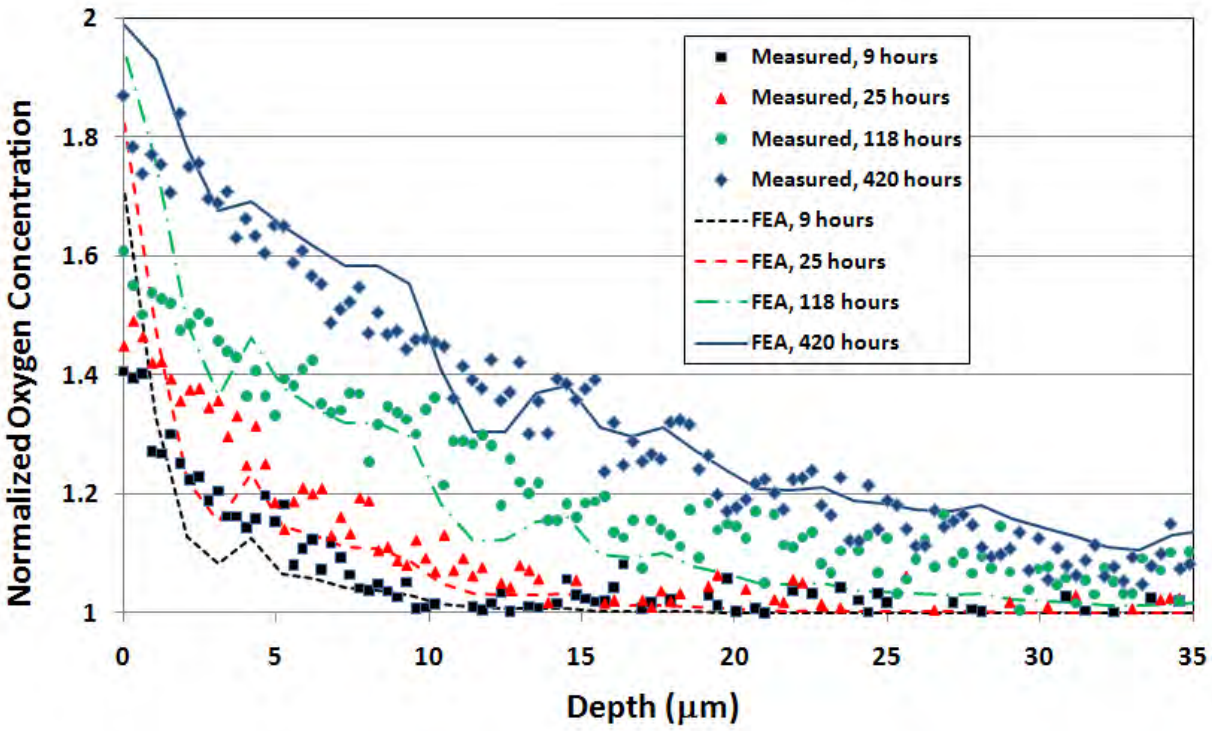

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